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(54) Title of the invention: Modified poly (p-xylylene) protection film and method of its production

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**Details**

**1.Title of the invention**

Modified poly (p-xylylene) protection film and method of its production.

**2. Scope of the claims**

(1) A corrosion resistant protection film obtained by heating one particular protection film from a group composed of poly (p-xylylene), poly (monochloro-p-xylylene) and poly (dichloro-p-xylylene) film in at least one of the following atmospheres, namely vacuum, inert gas and reducing gas, at a temperature above the glass transition temperature of the raw material mentioned above.

(2) It is a film obtained by heating poly (monochloro-p-xylylene) film in at least one of the following atmospheres, namely vacuum, inert gas and reducing gas, at a temperature above the glass transition temperature of the raw material mentioned above.

The intensity of X-ray diffraction peak / half bandwidth of this corrosion resistant protection film material observed around $14^{\circ}$ is more than 200.

(3) It is a film obtained by heating poly (p-xylylene) film, in at least one of the following atmospheres, namely vacuum, inert gas and reducing gas, at a temperature above the glass transition temperature of the raw material mentioned above.

The intensity of X-ray diffraction peak / half bandwidth of this corrosion resistant protection film material observed around 17° is more than 200.

(4) It is a film obtained by heating poly (dichloro-p-xylylene) film, in at least one of the following atmospheres, namely vacuum, inert gas and reducing gas, at a temperature above the glass transition temperature of the raw material mentioned above.

The intensity of X-ray diffraction peak / half bandwidth of this corrosion resistant protection film material observed around 13.5° is more than 200.

(5) Method of production of a corrosion resistant protection film obtained by heat-treating one particular protection film from a group composed of poly (p-xylylene), poly (monochloro-p-xylylene) and poly (dichloro-p-xylylene) film in at least one of the following atmospheres, namely vacuum, inert gas and reducing atmosphere, at a temperature above the glass transition temperature of the raw material mentioned above.

**3. Detailed description of the invention**

**[Fields of industrial usage]**

This invention is regarding a corrosion resistant protection film obtained by heat-treating poly (p-xylylene), poly (monochloro-p-xylylene) and poly (dichloro-p-xylylene) film in an inert atmosphere.

**[Conventional techniques]**

Recently, from the cost, mechanical fabricability and energy saving point of view, the rare earth type iron magnet, which is quite advantageous, has gained much attention. The iron magnet of rare earth type having 8 ~ 30% rare earth element, 2 ~ 28 % B and the balance as Fe (all in atomic ratio) is very well known. However, rare earth type iron magnet contains a large quantity of Nd and Fe that rust easily due to moisture and are likely to corrode easily due to chemicals like acids and alkalies. It is thus inferior to Sm-Co type magnet as far as corrosion is concerned. Coating of the magnets with a protection film of a polymer like poly (p-xylylene) is being studied. For example, in patent No. JP 55-103714, permanent magnets obtained by the method of coating the entire surface of magnet by vacuum evaporation method is mentioned.

**[The problems, this invention aims to solve]**

The drawback of the above-referred method is that the film does not show adequate adhesion to the magnet and is not sufficiently hard. Methods like coating by epoxy resin or fluorine based resin are also very well known, but the former lacks corrosion resistance and high baking temperature is necessary in case of fluorine based resin which may cause oxidation of the magnet.

Thus the objective of this invention is to offer a protection film with excellent corrosion resistance, adhesion and hardness, and also the production methods for such protection film.

The present inventors have applied for patents for invention regarding improvement of adhesion of poly (p-xylylene) film to a magnet by conducting plasma treatment on the magnet (application No. Hei 1-067521) and double coating of epoxy film (application No. Hei 1-141235) for improving the hardness of the film.

**[Measures for solving the problems]**

The present inventors investigated the flaws of the conventional techniques and observed that a film with excellent adhesion and hardness can be obtained by conducting heat treatment of poly (p-xylylyne) film under specific conditions. Thus this invention is about a corrosion resistant film obtained by heat-treating poly (p-xylylene) in at least one of the following atmospheres namely vacuum, inert gas and reducing gas, at a temperature above the glass transition temperature.

Poly (p-xylylyne) film used in this invention is the one with trade name "Parylene" manufactured by Union Carbide Co. and it includes poly monochloro substituted (monochloro-p-xylylene), dichloro-substituted poly (dichloro-p-xylylene) and non-substituted poly (p-xylylene). The example of poly (monochloro-p-xylylene) is considered below. From the viewpoint of productivity and rust prevention, the ideal thickness of the film is between 1 μm ~ 10 μm.

According to this invention, the resin film is heat-treated in any one of the atmospheres selected from the following, namely vacuum, inert gas or reducing gas. In an oxidizing atmosphere containing excess of oxygen, poly (monochloro-p-xylylene) gets oxidized and the film aimed at by this invention, cannot be obtained. It is desirable to use vacuum of $10^{-2}$ Torr or less. Rare gases like Argon, Neon, Krypton or Nitrogen can be used as inert gases while Hydrogen or Hydrogen/Argon gas can be used as the reducing gas. Any of the above atmospheres can be used without restriction.

In this invention, the above poly (monochloro-p-xylylene) film is heated at a temperature above the glass transition temperature, that is, above 80°C, preferably in the temperature range of 150 ~ 250°C. The heating period can vary from 0.5 ~ 3 hours and it is better to adjust it such that the intensity/half bandwidth measured by x-ray diffraction method described later lies in the specified range.

As regards the method of heating, there is no specific restriction, and methods like thermal conduction heating; fast infrared heating, high-frequency heating or microwave heating can be used. A vacuum drier or a vacuumized container can be used for creating the inert atmosphere.

In this way, the protection film can be obtained. It is better that the intensity/half bandwidth of the peak for this poly (monochloro-p-xylylene) protection film measured by X-ray diffraction method around 14° is 200 or more. If poly (p-xylylene) is used as the raw material, then the desirable value of intensity/half bandwidth of the peak measured in similar manner around 17° is about 200 or more. And when poly (p-xylylene) is used as the raw material, the desirable value of intensity/half bandwidth of the peak measured in similar manner around 13.5° is 200 or more.

The second part of this invention is the method of production of a corrosion resistant protection film obtained by heat-treating one particular protection film from a group composed of poly (p-xylylene), poly (monochloro-p-xylylene) and poly (dichloro-p-xylylene) in at least one of the following, namely vacuum, inert gas and reducing gas, at a temperature above the glass transition temperature of the raw material mentioned above.

In this method, first poly (monochloro-p-xylylene) film is prepared. Usually such a film can be prepared in the following manner. First, dimer of monochloro-p-xylylene is allowed to sublime by evaporating it in an evaporation furnace at a reduced pressure of 1 Torr or less. The glass-like dimer of monochloro-p-xylylene thus obtained is then introduced into a decomposition furnace and decomposed at 600 ~ 700° C at a pressure of around 0.5 Torr. This decomposed gas is then introduced into polymerization chamber and allowed to polymerize on the surface of the magnet at ordinary temperature under the condition of 0.01 ~ 0.1 Torr pressure. This operation can be carried out by using Parylene polymerization apparatus, Model 1010 (Manufactured by Union Carbide Co.).

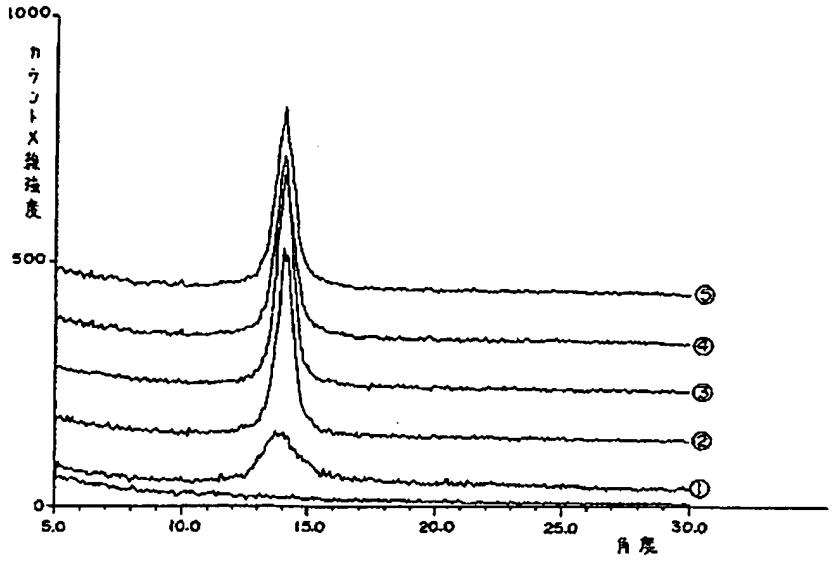
After this, poly (monochloro-p-xylylene) thus obtained is heated at a temperature above the glass transition temperature in one of the following atmospheres, namely vacuum, inert gas and reducing gas. The conditions like inert gas atmosphere, method of heating and period of heating are as mentioned above.

**[Action]**

The present inventors have observed that poly (monochloro-p-xylylene) is an excellent protection film material with excellent adhesion with metals and also excellent hardness, when heat-treated in an inert atmosphere. Although chemical structure of the protection film is not yet known clearly, however, it can be presumed from x-ray analysis that it is of more regular pattern. Fig.1 is a graph showing results of x-ray diffraction analysis of poly (monochloro-p-xylylene) film of this invention before heat treatment. No. (1) ~ (5) are the spectra for samples heat-treated under the conditions shown in Table 1. In Fig. 1, (1) is poly (monochloro-p-xylylene) film before heat treatment and it shows a peak around 14°. When, however, the heat treatment temperature exceeds 200°C, the peak becomes sharp and regularity of the film gets improved. From these results, it may be possible to specify the regular chemical structure of the heat-treated substance from the ratio of intensity of the peak and half width of the spectrum.

In this invention, satisfactory results are obtained in case of film hardness, adhesive property and corrosion resistance; as can be seen from the pencil hardness, cross-cut test, peeling test, moisture permeability and salt water spraying test, which may be attributed to the improved regular chemical structure mentioned above.

第1図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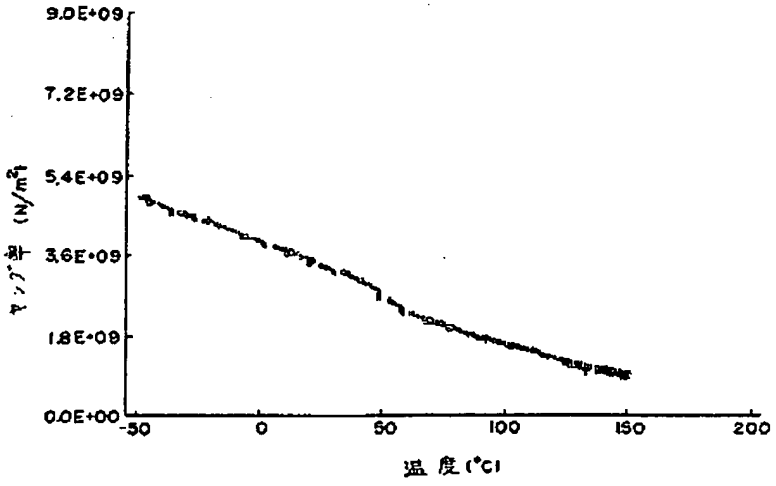
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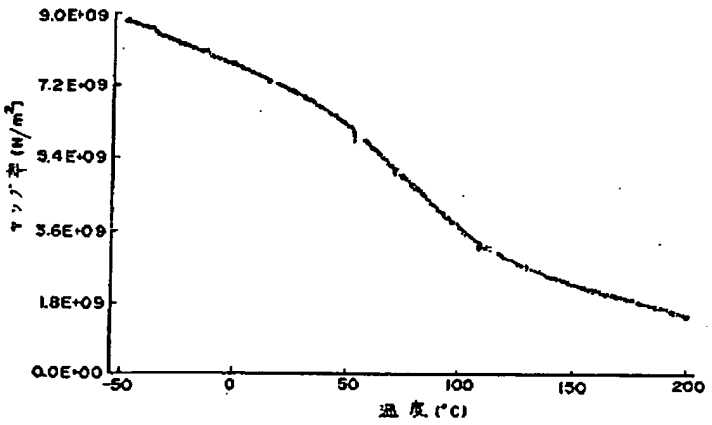
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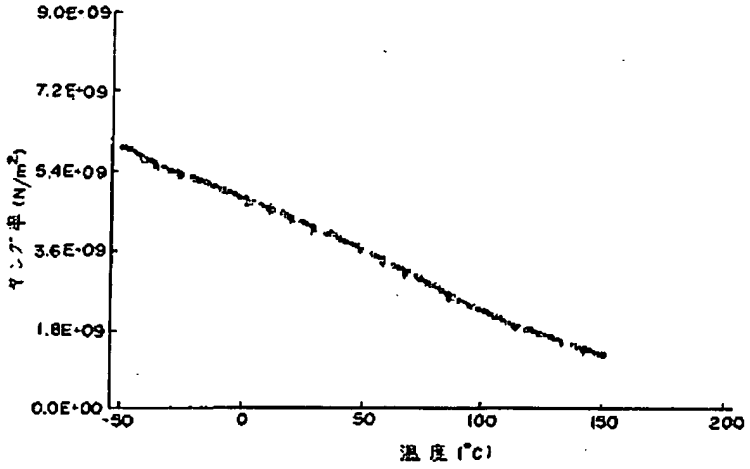
第4図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